

MODELING THE ELECTRON TRANSFER REACTION AT THE LITHIUM METAL ANODE-LIQUID ELECTROLYTE INTERFACE IN LITHIUM-AIR BATTERIES

Saeed Kazemiabnavi^a, Prashanta Dutta,^b and Soumik Banerjee^{b*}

^aDepartment of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136, United States

^bSchool of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164-2920, United States

*soumik.banerjee@wsu.edu

Introduction

The potentially much higher gravimetric energy storage density of lithium-air batteries compared to all other battery chemistries has made them promising energy storage systems for prevailing existing obstacles in large scale applications.¹ The most important application drawing attention is transportation systems in which the gravimetric energy density and safety become very challenging. Moreover, lithium-air batteries can also have significant impact on energy storage systems in other areas such as consumer electronics and robotic uses.

One of the crucial criteria in the abovementioned applications is safety, which may not be easily achieved due to the usage of extremely flammable organic solvents as the electrolyte in conventional lithium batteries. Therefore, it is extremely important to identify novel electrolytes for development of safe lithium-air batteries. However, the performance of these batteries is extremely sensitive to the electrochemical stability and physicochemical properties of the electrolytes. Due to their interesting characteristics such as relatively wide electrochemical stability window and very low vapor pressure, ionic liquid solvents can play a crucial role as electrolytes for enhancing the cyclic performance and safety of lithium-air batteries.² One of the principle performance characteristics of a lithium-air battery is the current density at electrodes, which is determined by the electron transfer (ET) rates for the electrochemical reactions at the surface of the electrodes. This study reports calculations of the electron transfer rate constant for the electrochemical oxidation of lithium metal into Li⁺ ion at the anode. The effect of static dielectric constant of the electrolyte on the thermodynamics and kinetics of this reaction is also investigated.

Theoretical Framework

In this study, a novel method based on Marcus theory³ is carried out to calculate the electron transfer rate constant for the oxidation of lithium metal. The mathematical expression of the Marcus equation is:

$$k_{et} = \frac{2\pi}{\hbar} |V_{RP}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_B T}\right) \quad (1)$$

where k_{et} is the rate constant for electron transfer, $|V_{RP}|$ is the electronic coupling between the initial and final states, λ is the reorganization energy (both inner and outer sphere), and ΔG° is the total Gibbs free energy change for the electron transfer reaction. k_B is the Boltzmann constant and T is the absolute temperature.

Built on the Arrhenius equation for the chemical reaction rates, the Marcus theory provides a mathematical expression for the activation energy as a function of the reorganization energy and Gibbs free energy as shown in Eq. (2).

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \quad (2)$$

Moreover, the Marcus equation also provides a mathematical expression for the pre-factor, which is a function of electronic coupling energy and reorganization energy.

Methodology

Lithium metal has a BCC structure with a lattice constant of 3.507 Å. The structure was optimized for both neutral and negatively charged lithium lattice. Each electron released by a lithium atom in the lattice was distributed over the remaining lithium atoms creating a positively charged lithium ion and negatively charged lattice.^{4, 5} The method of Corresponding Orbital Transformation was utilized to calculate the electronic coupling energy using the initial and final wave functions.^{6, 7} Moreover, the Conductor-like Screening Model⁸ (COSMO solvation model) was implemented to account for the effect of the dielectric constant of the ionic liquid electrolyte on the reaction rate constants.

Density Functional Theory (DFT) with B3LYP exchange-correlation functional^{9, 10} was utilized with 6-311++G** as the basis set applying polarization and diffuse on all atoms to calculate the free energies of all the involved chemical species in the presence of implicitly defined ionic liquid electrolyte using COSMO solvation model. Periodic boundary condition DFT with revised Perdew, Burke, and Ernzerhof¹¹ (revPBE) GGA functional and 6-31++G* basis set^{12, 13} was used for the optimization of the lithium lattice. All calculations were carried out using NWChem 6.1 computational chemistry software package.¹⁴

Results and Discussion

In this study 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C_nMIM⁺ TFSI⁻) ionic liquids, with varying static dielectric constants due to varying number of carbon atoms in the side alkyl chain, were chosen as model electrolytes.¹⁵ Figure 1 shows the variation of the electron transfer rate constant and the change in the Gibbs free energy of the electrochemical oxidation of lithium metal in various ionic liquid electrolytes with different static dielectric constants. The obtained results indicate that the magnitude of the thermodynamic driving force for the anodic reaction increases with increase in the static dielectric constant of the electrolyte. Moreover, it is observed that the electron transfer rate constant for the anodic reaction can be directly related to the static dielectric constant of the ionic liquid. Therefore, the oxidation of lithium metal is both thermodynamically and kinetically favorable in electrolytes with higher static dielectric constant.

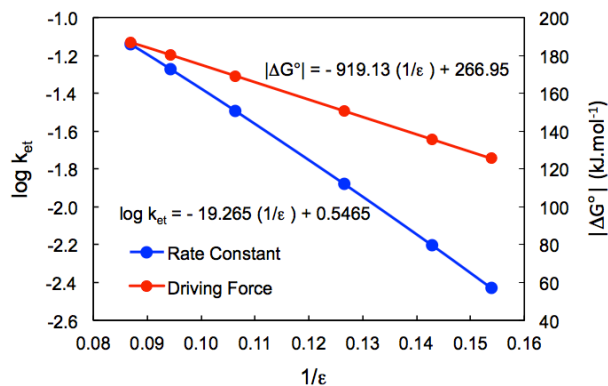


Figure 1. The variation of the ET rate constant and the magnitude of the driving force with the static dielectric constant of the ionic liquid electrolyte are shown.

Conclusions

Using DFT calculation, it is observed that the reaction rate constant and magnitude of the driving force of the oxidation of lithium metal into Li^+ ions at the anode in lithium-air batteries increase with increase in the static dielectric constant of the electrolyte.

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